

LIGHT LITHOPHILE ELEMENTS IN NATURAL AND EXPERIMENTAL PHASES IN MARTIAN BASALTS: IMPLICATIONS FOR THE DEGASSING OF WATER FROM MARTIAN MAGMAS. C. D. K. Herd¹, A. H. Treiman¹, G. A. McKay² and C. K. Shearer³, ¹Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058, herd@lpi.usra.edu, ²Astromaterials Research Office, SR, NASA Johnson Space Center, Houston, TX 77058, ³Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131.

Introduction: Lentz et al. [1] argued that zoning trends in light lithophile elements (LLE) in pyroxene in Shergotty and Zagami are evidence for the degassing of magmatic water. We tested this inference by obtaining: additional LLE analyses of Shergotty and Zagami pyroxene; analyses of Pasamonte pyroxene; and silicate and phosphate partition coefficients for B and Li for martian magma and mineral compositions.

Analytical Details: Phases in natural samples and experimental charges were analyzed by electron microprobe for major and minor elements, and by ion probe for the LLE, using the Cameca SX-100 electron microprobe at the Johnson Space Center (JSC) and the Cameca IMS 4f ion probe at the University of New Mexico (UNM), respectively. Ion probe analyses of experimental charges included ⁷B, ¹¹Li and ³⁰Si. Analyses of natural phases also included ⁹Be for Zagami and Pasamonte, and ⁹Be, ⁴²Ca, ⁴⁸Ti and ¹⁴⁰Ce for Shergotty. Other analytical details are as described in [2]. LLE standards for ion probe analyses were assembled from several sources, including Dr. Jeff Ryan (USF); many of these are the same as used by [1]. A homogeneous apatite grain from the Richardson (Fission) Mine in Wilberforce, Ontario, Canada, was developed as a Li and B standard for the analysis of phosphates.

Experimental Details: Experiments were carried out in order to determine whether the observed decrease in Li and B in pyroxene could be explained by the uptake of these elements by other minerals. One-atmosphere, Re-loop gas-mixing experiments were performed in Deltech furnaces at JSC. A starting composition approximating that of QUE 94201 was doped with lithium tetraborate (Li₂B₄O₇), yielding ~500 ppm Li and 1600 ppm B. By varying run temperatures, we were able to grow olivine, pyroxene and plagioclase. Adding P₂O₅ enabled the crystallization of merrillite, a phosphate mineral. Other experimental details follow [2].

Diffusion of Li and B from melt to furnace gas was observed, and we quantified this effect through an additional series of experiments. Losses of B and Li below the liquidus (~1170°C) are not significant, and the use of Re loops enabled the homogenization time (at 1300°C), where loss is greatest, to be minimized.

LLE in Shergotty and Zagami: Pyroxene grains in Shergotty (UNM 411) and Zagami (UNM 991) were characterized by EMP prior to SIMS analysis. The Shergotty pyroxenes that we analyzed cover the entire range of previously reported Fs contents [3]. The Zagami pyroxenes that we analyzed cover most of the previously reported range [3], and appear to include more Mg-rich (lower Ti) compositions than those analyzed by [1].

Our results for Li and B in Shergotty and Zagami pyroxene are compared to those of [1] in Figure 1. Be (not shown) correlates with Ti in both samples [1] as expected from its incompatible behavior in pyroxene. Our results for Shergotty show a slight negative correlation between B and Ti, although the scatter in the data precludes definitive interpretation. The data of [1] show a much stronger negative correlation between B and Ti in Shergotty. Our results from Zagami show a slight positive correlation between B and Ti, whereas B from [1], although scattered, is relatively flat relative to Ti when all points are considered.

The greatest agreement between the two datasets is in Li vs. Ti. Both Zagami datasets show a decrease in Li with Ti, and in Shergotty, the slope of the line-of-best-fit for our data is nearly identical to that for the data of [1]. Therefore, our results corroborate those of [1]: Li in pyroxene undergoes a decrease from early pyroxene to late pyroxene.

LLE in Pasamonte: Pasamonte is an unequilibrated eucrite, an asteroidal basalt formed from a magma derived from shallow depths. No water was involved in its igneous petrogenesis.

Our results from the analysis of Pasamonte pyroxene show a positive correlation between each of the LLE and Ti, demonstrating that, under anhydrous conditions, Li, Be and B behave incompatibly with respect to pyroxene.

Results of partitioning experiments: D values for Li and B in pyroxene, plagioclase, olivine, and merrillite, along with ranges in composition, are given in Table 1, with results of previous (terrestrial) work [4,5] for comparison.

The results demonstrate that Li and B are incompatible in all of the phases investigated. Therefore, the crystallization of these phases cannot account for a core-to-rim decrease in Li and B in the pyroxene. This

is confirmed by the results of the experiments in which pyroxene major-element zoning reflects the onset of plagioclase crystallization [2]; in such cases, Li and B increase or remain unchanged from core to rim.

Implications for magmatic water in martian basalts: We modeled the crystallization of Shergotty and Zagami and the partitioning of Li and B into the phases using the D values derived from the experiments (Table 1), and calculate that the pyroxene rims in both basalts should have 3 times more Li and B than the pyroxene cores. It should be noted that the scatter in our data for B in pyroxene for both Zagami and Shergotty is approximately a factor of three. Modeling also shows that in order to explain the observed decrease (~70%) in Li from core to rim, the D_{Li} for pyroxene would have to be at least 1.2, a value not supported by our experimental results, or those of others (Table 1).

The results of our analyses of natural and experimental samples and modeling of Li partitioning are consistent with the hypothesis of [1] that degassing of magmatic water removed Li from Shergotty and Zagami as they were crystallizing. Further experimental work to determine whether Li partitions readily into hydrous fluids in equilibrium with basaltic melt is required to prove the validity of this hypothesis.

Boron partitioning has been examined experimentally by Hervig et al. [6]. These authors demonstrated that $D(\text{fluid-melt})$ for B in basaltic melt (MORB) is less than one, demonstrating that B is not always strongly extracted from melts into hydrous fluids at magmatic temperatures. This result helps to explain the observed B zoning trends in Shergotty and Zagami pyroxene: if magmatic degassing occurred, as appears to be indicated by Li zoning, then B may have been incompatible with respect to the fluid (i.e. remained in the melt) and also incompatible with respect the crystallizing phases.

References: [1] Lentz R. C. F. et al. (2001) *GCA*, 65, 4551-4565. [2] Herd C. D. K. et al. (2002) *LPS XXXIII*, Abstract #1333. [3] Meyer, C. (1998) *Mars Meteorite Compendium*, NASA-JSC, Houston, TX. [4] Brenan et al. (1988) *GCA*, 62, 2129-2141 [5] Ryan J. G. (1989) Ph.D. Dissertation, Columbia Univ. [6] Hervig et al. (2002) *Am. Mineral.*, 87, 769-774.

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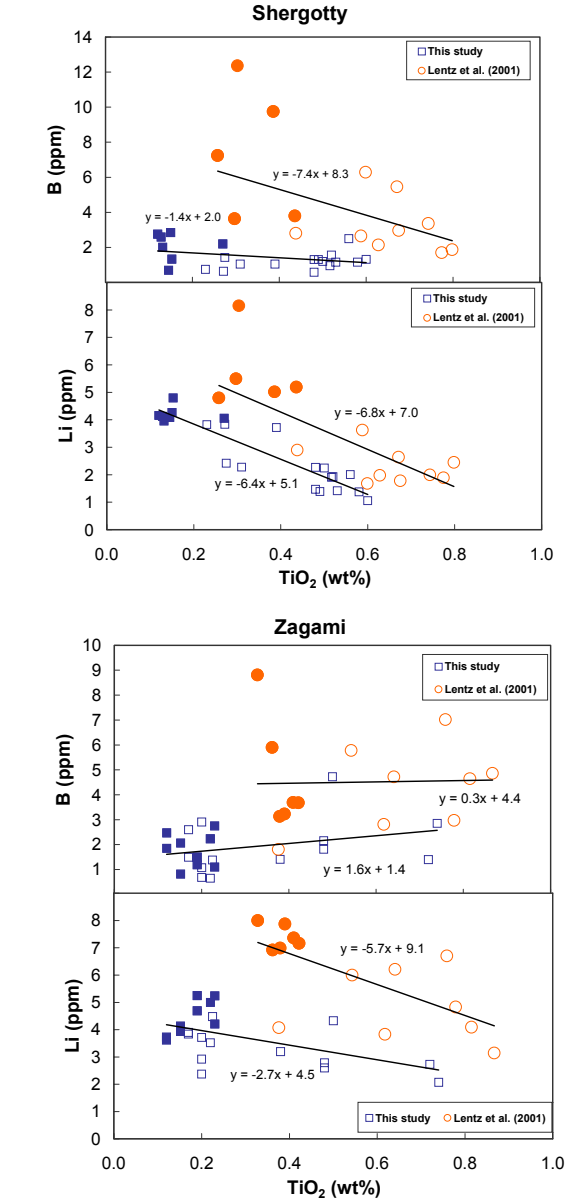


Figure 1. Li and B versus TiO₂ in Shergotty and Zagami pyroxene. Cores are denoted by filled symbols.

Table 1. D values from experiments compared with literature values. The composition of experimental merrillite is $\text{Ca}_9\text{Na}_{0.1}(\text{Fe}_{0.4}\text{Mg}_{0.8})(\text{PO}_4)_7$.

Mineral	Composition	D_{Li}	D_B
Pyroxene	$\text{Wo}_{19-44}\text{Fs}_{17-39}$	0.20(3)	0.024(9)
Pyroxene[4]	$\text{Wo}_{52}\text{En}_{48}$	0.20(3)	0.016(2)
Olivine	Fo_{57-51}	0.27(1)	0.007(1)
Olivine[4]	Fo_{100}	0.15(2)	0.006(2)
Plagioclase	Ab_{15}	0.48(4)	0.024(5)
	Ab_{30-34}	0.37(4)	
Plagioclase[5]	Not given	0.23	0.05
Merrillite	--	0.70(1)	0.03(1)